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(54) **Coated detergent tablet**

(57) The present invention relates to a coated detergent tablet, the coating comprising an acid having a

melting temperature of at least 145°C, whereby the coating further comprises a clay.

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## Description

[0001] The present invention relates to coated detergent tablets, especially those adapted for use in washing machines, and to processes for making the coated detergent tablets.

[0002] Although cleaning compositions in tablet form have often been proposed, these have not (with the exception of soap bars for personal washing) gained any substantial success, despite the several advantages of products in a unit dispensing form. One of the reasons for this may be that detergent tablets require a relatively complex manufacturing process. In particular, it is often desirable to provide the tablet with a coating and this adds to the difficulties of manufacture.

While tablets without a coating are entirely effective in use, they usually lack the necessary surface hardness to withstand the abrasion that is a part of normal manufacture, packaging and handling. The result is that non-coated tablets suffer from abrasion during these processes, resulting in chipped tablets and loss of active material.

[0003] Finally, coating of tablets is often desired for aesthetic reasons, to improve the outer appearance of the tablet or to achieve some particular aesthetic effect. Numerous methods of tablet coating have been proposed, and many of these have been suggested for detergent tablets. However, all of these methods have certain disadvantages, as will be explained below.

[0004] GB-A-0 989 683, published on 22nd April 1965, discloses a process for preparing a particulate detergent from surfactants and inorganic salts: spraying on water-soluble silicate; and pressing the detergent particles into a solid form-retaining tablet. Finally a readily water-soluble organic film-forming polymer (for example, polyvinyl alcohol) provides a coating to make the detergent tablet resistant to abrasion and accidental breakage.

[0005] EP-A-0 002 293, published on 13th June 1979, discloses a tablet coating comprising hydrated salt such as acetate, metaborate, orthophosphate, tartrate, and sulphate.

[0006] EP-A-0 716 144, published on 12th June 1996, also discloses laundry detergent tablets with water-soluble coatings which may be organic polymers including acrylic/maleic co-polymer, polyethylene glycol, PVPVA, and sugar.

[0007] WO9513215, published on 6th July 1995, provides water-insoluble coatings for solid cast tablets. The tablets are provided with hydrophobic coatings including wax, fatty acid, fatty acid amides, and polyethylene glycol.

[0008] EP-A-0 846 754, published on the 10th of June 1998, provides a tablet having a coating comprising a dicarboxylic acid, the coating material typically having a melting point of from 40°C to 200°C.

[0009] EP-A-0 846 755, published on the 10th of June 1998, provides a tablet having a coating comprising a material insoluble in water at 25°C, such as C12-C22 fatty acids, adipic acid or C8-C13 dicarboxylic acids.

[0010] EP-A-0 846 756, published on the 10th of June 1998, provides a tablet having a coating comprising a disintegrant material and preferably an effervescent material.

[0011] The present invention provides a means by which coated tablets can be provided with a coating so that they can be stored, shipped and handled without damage, the coating being easily broken when the tablet is in the washing machine, releasing the active ingredients into the wash solution.

[0012] The object of the present invention is to provide a tablet having a coating which is sufficiently hard to protect the tablet from mechanical forces when stored, shipped and handled, and disperses readily in an aqueous solution.

## Summary of the Invention

[0013] The object of the invention is achieved by providing a coated detergent tablet, the coating comprising an acid having a melting temperature of at least 145°C, whereby the coating further comprises a clay.

## Detailed Description of the Invention

## Coating

[0014] Solidity of a tablet may be improved by making a coated tablet, the coating covering a non-coated tablet, thereby further improving the mechanical characteristics of the tablet while maintaining or further improving dissolution. This very advantageously applies to multi-layer tablets, whereby the mechanical characteristics of a more elastic layer can be transmitted via the coating to the rest of the tablet, thus combining the advantage of the coating with the advantage of the more elastic layer. Indeed, mechanical constraints will be transmitted through the coating, thus improving mechanical integrity of the tablet.

In one embodiment of the present invention, the tablets may then be coated so that the tablet does not absorb moisture, or absorbs moisture at only a very slow rate. The coating is also strong so that moderate mechanical shocks to which the tablets are subjected during handling, packing and shipping result in no more than very low levels of breakage or attrition. Finally the coating is preferably brittle so that the tablet breaks up quickly when subjected to stronger mechanical shock. Furthermore it is advantageous if the coating material is dissolved under alkaline conditions, or is

readily emulsified by surfactants. This contributes to avoiding the problem of visible residue in the window of a front-loading washing machine during the wash cycle, and also avoids deposition of undissolved particles or lumps of coating material on the laundry load.

Water solubility is measured following the test protocol of ASTM E1146-87 entitled, "Standard Test Method for Measurements of Aqueous Solubility".

The coating material has a melting point preferably of from 40 °C to 200 °C. The coating can be applied in a number of ways. Two preferred coating methods are a) coating with a molten material and b) coating with a solution of the material.

In a), the coating material is applied at a temperature above its melting point and solidifies on the tablet. In b), the coating is applied as a solution, the solvent being dried to leave a coherent coating. The substantially insoluble material can be applied to the tablet by, for example, spraying or dipping. Normally when the molten material is sprayed on to the tablet, it will rapidly solidify to form a coherent coating. When tablets are dipped into the molten material and then removed, the rapid cooling again causes rapid solidification of the coating material. During the solidification phase, the coating undergoes some internal stress (e.g. shrinkage upon cooling) and external stress (e.g. tablet relaxation). This will likely cause some cracks in the structure such as edge splitting if the coating material is too brittle to withstand these mechanical stresses, which is the case when a coating is solely made from components solid at 25°C. Indeed, it is preferred that the coating comprises a component which is liquid at 25°C. It is believed that this liquid component will allow the coating to better withstand and absorb mechanical stress by rendering the coating structure more flexible. The component which is liquid at 25°C is preferably added to the coating materials in proportions of less than 10% by weight of the coating, more preferably less than 5% by weight, and most preferably of less than 3% by weight. The component which is liquid at 25°C is preferably added to the coating materials in proportions of more than 0.1% by weight of the coating, more preferably more than 0.3% by weight, and most preferably of more than 0.5% by weight. Further preferred is the addition of reinforcing fibres to the coating in order to further reinforce the structure.

**[0015]** Preferably, the coating comprises a crystallised structure. By crystallised, it should be understood that the coating comprises a material which is solid at ambient temperature (25°C) and has a structure exhibiting some order. This can be detected typically by usual crystallography techniques e.g. X-ray analysis, on the material itself. In a more preferred embodiment, the material forming the crystallised structure does not co-crystallise or only partially with the optional component which is liquid at 25°C mentioned above. Indeed, it is preferred that the optional component remains in the liquid state at 25°C in the coating crystalline structure in order to provide flexibility to the structure and resistance to mechanical stress. In another embodiment, the optional component which is liquid at 25°C may advantageously have a functionality in the washing of laundry, for example silicone oil which provides suds suppression benefits or perfume oil.

**[0016]** The coating comprises materials other than the optional component which is liquid at 25°C. Suitable coating materials are for example dicarboxylic acids. Particularly suitable dicarboxylic acids are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid and mixtures thereof. Most preferred is adipic acid. Clearly substantially insoluble materials having a melting point below 40 °C are not sufficiently solid at ambient temperatures and it has been found that materials having a melting point above about 200 °C are not practicable to use. Preferably, an acid having a melting point of more than 90°C such as azelaic, sebacic acid, dodecanedioic acid. According to the invention, it was found that an acid having a melting point of more than 145°C such as adipic acid was found particularly suitable.

**[0017]** By "melting point" is meant the temperature at which the material when heated slowly in, for example, a capillary tube becomes a clear liquid.

A coating of any desired thickness can be applied according to the present invention. For most purposes, the coating forms from 1% to 10% preferably from 1.5% to 5% of the tablet weight.

Tablet coatings are very hard and provide extra strength to the tablet.

Examples of optional components which are liquid at 25° are including PolyEthylene Glycols, thermal oil, silicon oil, esters of dicarboxylic acids, mono carboxylic acids, paraffin, triacetin, perfumes or alkaline solutions. It is preferred that the structure of the components which is liquid at 25°C is close to the material forming the crystallised structure, so that the structure is not excessively disrupted. In a most preferred embodiment, the crystallised structure is made of adipic acid, the component which is liquid at 25°C being available under the name Coasol™ from Chemoxy International, being a blend of the di-isobutyl esters of the glutaric, succinic and adipic acid. The advantage of the use of this component being the good dispersion in the adipic acid to provide flexibility. It should be noted that disintegration of the adipic acid is further improved by the adipate content of Coasol™.

**[0018]** Fracture of the coating in the wash can be improved by adding a disintegrant in the coating. This disintegrant will swell once in contact with water and break the coating in small pieces. This will improve the dissolution of the coating in the wash solution. The disintegrant is suspended in the coating melt at a level of up to 30%, preferably between 5% and 20%, most preferably between 5 and 10% by weight. Possible disintegrants are described in Handbook

of Pharmaceutical Excipients (1986). Examples of suitable disintegrants include starch, natural, modified or pregelatinized starch, sodium starch gluconate, gum, agar gum, guar gum, locust bean gum, karaya gum, pectin gum, tragacanth gum, croscarmellose Sodium, crospovidone, cellulose, carboxymethyl cellulose, alginic acid and its salts including sodium alginate, silicone dioxide, clay, polyvinylpyrrolidone, soy polysaccharides, ion exchange resins, polymers containing cationic (e.g. quaternary ammonium) groups, amine-substituted polyacrylates, polymerised cationic amino acids such as poly-L-lysine, polyallylamine hydrochloride) and mixtures thereof.

**[0019]** According to the invention, the coating comprises an acid having a melting temperature of at least 145°C such as adipic acid for example, as well as a clay, such as a bentonite clay for example, whereby the clay is used as a disintegrant and also to render the structure of adipic acid more favourable for water penetration, thus improving the dispersion of the adipic acid in an aqueous medium. Preferred are clays having a particle size of less than 75 µm, more preferably of less than 53 µm, in order to obtain the desired effect on the structure of the acid. Preferred are bentonite clays. Indeed the acid has a melting point such that traditional cellulosic disintegrants undergo a thermal degradation during the coating process, whereas such clays are found to be more heat stable. Further, traditional cellulosic disintegrant such as Nymcel<sup>TM</sup> for example are found to turn brown at these temperatures.

**[0020]** In another preferred embodiment, the coating further comprises reinforcing fibres. Such fibres have been found to improve further the resistance of the coating to mechanical stress and minimise the splitting defect occurrence. Such fibres are preferably having a length of at least 100 µm, more preferably of at least 200 µm and most preferably of at least 250 µm to allow structure reinforcement. Such fibres are preferably having a length of at less than 500 µm, more preferably of less than 400 µm and most preferably of less than 350 µm in order not to impact onto dispersion of the coating in an aqueous medium. Materials which may be used for these fibres include viscose rayon, natural nylon, synthetic nylon (polyamides types 6 and 6.6), acrylic, polyester, cotton and derivatives of cellulose such as CMCs. Most preferred is a cellulosic material available under the trade mark Solka-Floc<sup>TM</sup> from Fibers Sales & Development. It should be noted that such fibres do not normally need precompression for reinforcing the coating structure. Such fibres are preferably added at a level of less than 5% by weight of the coating, more preferably less than 3% by weight. Such fibres are preferably added at a level of more than 0.5% by weight of the coating, more preferably more than 1% by weight.

**[0021]** A preferred process for making a tablet according to the invention comprises the steps of:

- (a) forming a core by compressing a particulate material, the particulate material comprising surfactant and detergent builder;
- (b) applying a coating material to the core, the coating material being in the form of a melt;
- (c) allowing the molten coating material to solidify;

characterised in that the coating comprising an acid having a melting temperature of at least 145°C, whereby the coating further comprises a clay.

**[0022]** Another preferred process for making a tablet according to the invention comprises the steps of:

- (a) forming a core by compressing a particulate material, the particulate material comprising surfactant and detergent builder;
- (b) applying a coating material to the core, the coating material being dissolved in a solvent or water;
- (c) allowing the solvent or water to evaporate;

characterised in that the coating comprising an acid having a melting temperature of at least 145°C, whereby the coating further comprises a clay.

**[0023]** The tablets may comprise components such as fragrance, surfactants, enzymes, detergent etc.... Typical tablet compositions for the preferred embodiment of the present invention are disclosed in the pending European applications of the Applicant n° 96203471.6, 96203462.5, 96203473.2 and 96203464.1 for example. Elements typically entering in the composition of detergent tablets or of other forms of detergents such as liquids or granules are detailed in the following paragraphs.

#### Highly soluble Compounds

**[0024]** The tablet may comprise a highly soluble compound. Such a compound could be formed from a mixture or from a single compound. A highly soluble compound is defined as follow:

A solution is prepared as follows comprising de-ionised water as well as 20 grams per litre of a specific compound:

- 1- 20 g of the specific compound is placed in a Sotax Beaker. This beaker is placed in a constant temperature bath set at 10°C. A stirrer with a marine propeller is placed in the beaker so that the bottom of the stirrer is at 5

- mm above the bottom of the Sotax beaker. The mixer is set at a rotation speed of 200 turns per minute
- 2- 980 g of the de-ionised water is introduced into the Sotax beaker.
  - 3- 10 s after the water introduction, the conductivity of the solution is measured, using a conductivity meter.
  - 4- Step 3 is repeated after 20, 30, 40, 50, 1min, 2 min, 5 min and 10 min after step 2.
  - 5- The measurement taken at 10 min is used as the plateau value or maximum value

The specific compound is highly soluble according to the invention when the conductivity of the solution reaches 80% of its maximum value in less than 10 seconds, starting from the complete addition of the de-ionised water to the compound. Indeed, when monitoring the conductivity in such a manner, the conductivity reaches a plateau after a certain period of time, this plateau being considered as the maximum value. Such a compound is preferably in the form of a flowable material constituted of solid particles at temperatures comprised between 10 and 80°Celsius for ease of handling, but other forms may be used such as a paste or a liquid.

Example of highly soluble compounds include Sodium di isoalkylbenzene sulphonate (DIBS) or Sodium toluene sulphonate

#### Cohesive Effect

**[0025]** The tablet may comprise a compound having a Cohesive Effect on the particulate material of a detergent matrix forming the tablet. The Cohesive Effect on the particulate material of a detergent matrix forming the tablet or a layer of the tablet is characterised by the force required to break a tablet or layer based on the examined detergent matrix pressed under controlled compression conditions. For a given compression force, a high tablet or layer strength indicates that the granules stuck highly together when they were compressed, so that a strong cohesive effect is taking place. Means to assess tablet or layer strength (also refer to diametrical fracture stress) are given in *Pharmaceutical dosage forms: tablets* volume 1 Ed. H.A. Lieberman et al. published in 1989.

The cohesive effect is measured by comparing the tablet or layer strength of the original base powder without compound having a cohesive effect with the tablet or layer strength of a powder mix which comprises 97 parts of the original base powder and 3 parts of the compound having a cohesive effect. The compound having a cohesive effect is preferably added to the matrix in a form in which it is substantially free of water (water content below 10% (pref. below 5%)). The temperature of the addition is between 10 and 80°C, more pref. between 10 and 40°C.

A compound is defined as having a cohesive effect on the particulate material according to the invention when at a given compacting force of 3000N, tablets with a weight of 50g of detergent particulate material and a diameter of 55mm have their tablet tensile strength increased by over 30% (preferably 60 and more preferably 100%) by means of the presence of 3% of the compound having a cohesive effect in the base particulate material.

An example of a compound having a cohesive effect is Sodium di isoalkylbenzene sulphonate.

When integrating a highly soluble compound having also a cohesive effect on the particulate material used for a tablet or layer formed by compressing a particulate material comprising a surfactant, the dissolution of the tablet or layer in an aqueous solution is significantly increased. In a preferred embodiment, at least 1% per weight of a tablet or layer is formed from the highly soluble compound, more preferably at least 2%, even more preferably at least 3% and most preferably at least 5% per weight of the tablet or layer being formed from the highly soluble compound having a cohesive effect on the particulate material.

It should be noted that a composition comprising a highly soluble compound as well as a surfactant is disclosed in EP-A-0 524 075, this composition being a liquid composition.

A highly soluble compound having a cohesive effect on the particulate material allows to obtain a tablet having a higher tensile strength at constant compacting force or an equal tensile strength at lower compacting force when compared to traditional tablets. Typically, a whole tablet will have a tensile strength of more than 5kPa, preferably of more than 10kPa, more preferably, in particular for use in laundry applications, of more than 15kPa, even more preferably of more than 30 kPa and most preferably of more than 50 kPa, in particular for use in dish washing or auto dish washing applications; and a tensile strength of less than 300 kPa, preferably of less than 200 kPa, more preferably of less than 100 kPa, even more preferably of less than 80 kPa and most preferably of less than 60 kPa. Indeed, in case of laundry application, the tablets should be less compressed than in case of auto dish washing applications for example, whereby the dissolution is more readily achieved, so that in a laundry application, the tensile strength is preferably of less than 30 kPa.

This allows to produce tablets or layers which have a solidity and mechanical resistance comparable to the solidity or mechanical resistance of traditional tablets while having a less compact tablet or layer thus dissolving more readily. Furthermore, as the compound is highly soluble, the dissolution of the tablet or layer is further facilitated, resulting in a synergy leading to facilitated dissolution for a tablet according to the invention.

## Tablet Manufacture

[0026] The tablet may comprise several layers. For the purpose of manufacture of a single layer, the layer may be considered as a tablet itself.

Detergent tablets can be prepared simply by mixing the solid ingredients together and compressing the mixture in a conventional tablet press as used, for example, in the pharmaceutical industry. Preferably the principal ingredients, in particular gelling surfactants, are used in particulate form. Any liquid ingredients, for example surfactant or suds suppressor, can be incorporated in a conventional manner into the solid particulate ingredients.

In particular for laundry tablets, the ingredients such as builder and surfactant can be spray-dried in a conventional manner and then compacted at a suitable pressure. Preferably, the tablets according to the invention are compressed using a force of less than 100000N, more preferably of less than 50000N, even more preferably of less than 5000N and most preferably of less than 3000 N. Indeed, the most preferred embodiment is a tablet suitable for laundry compressed using a force of less than 2500N, but tablets for auto dish washing may also be considered for example, whereby such auto dish washing tablets are usually more compressed than laundry tablets.

The particulate material used for making a tablet can be made by any particulation or granulation process. An example of such a process is spray drying (in a co-current or counter current spray drying tower) which typically gives low bulk densities 60Cg/l or lower. Particulate materials of higher density can be prepared by granulation and densification in a high shear batch mixer/granulator or by a continuous granulation and densification process (e.g. using Lodige® CB and/or Lodige® KM mixers). Other suitable processes include fluid bed processes, compaction processes (e.g. roll compaction), extrusion, as well as any particulate material made by any chemical process like flocculation, crystallisation, sintering, etc. Individual particles can also be any other particle, granule, sphere or grain.

The components of the particulate material may be mixed together by any conventional means. Batch is suitable, for example, a concrete mixer, Nauta mixer, ribbon mixer or any other. Alternatively the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in one or more drum(s) or mixer(s). Non-gelling binder can be sprayed on to the mix of some, or all of, the components of the particulate material. Other liquid ingredients may also be sprayed on to the mix of components either separately or premixed. For example perfume and slurries of optical brighteners may be sprayed. A finely divided flow aid (dusting agent such as zeolites, carbonates, silicas) can be added to the particulate material after spraying the binder, preferably towards the end of the process, to make the mix less sticky.

The tablets may be manufactured by using any compacting process, such as tableting, briquetting, or extrusion, preferably tableting. Suitable equipment includes a standard single stroke or a rotary press (such as Courtoy®, Korch®, Manesty®, or Bonals®). The tablets prepared according to this invention preferably have a diameter of between 20mm and 60mm, preferably of at least 35 and up to 55 mm, and a weight between 25 and 100 g. The ratio of height to diameter (or width) of the tablets is preferably greater than 1:3, more preferably greater than 1:2. The compaction pressure used for preparing these tablets need not exceed 100000 kN/m<sup>2</sup>, preferably not exceed 30000 kN/m<sup>2</sup>, more preferably not exceed 5000 kN/m<sup>2</sup>, even more preferably not exceed 3000kN/m<sup>2</sup> and most preferably not exceed 1000kN/m<sup>2</sup>. In a preferred embodiment according to the invention, the tablet has a density of at least 0.9 g/cc, more preferably of at least 1.0 g/cc and preferably of less than 2.0 g/cc, more preferably of less than 1.5 g/cc, even more preferably of less than 1.25 g/cc and most preferably of less than 1.1 g/cc.

Multilayered tablets are typically formed in rotating presses by placing the matrices of each layer, one after the other in matrix force feeding flasks. As the process continues, the matrix layers are then pressed together in the precompression and compression stages stations to form the multilayer layer tablet. With some rotating presses it is also possible to compress the first feed layer before compressing the whole tablet.

## Hydrotrope compound

[0027] A highly soluble compound having a cohesive effect may be integrated to a detergent tablet, whereby this compound is also a hydrotrope compound. Such hydrotrope compound may be generally used to favour surfactant dissolution by avoiding gelling. A specific compound is defined as being hydrotrope as follows (see S.E. Friberg and M. Chiu J Dispersion Science and Technology, 9(5&6), pages 443 to 457, (1988-1989)):

1. A solution is prepared comprising 25% by weight of the specific compound and 75% by weight of water.
2. Octanoic Acid is thereafter added to the solution in a proportion of 1.6 times the weight of the specific compound in solution, the solution being at a temperature of 20°Celsius. The solution is mixed in a Sotax beaker with a stirrer with a maximum propeller, the propeller being situated at about 5mm above the bottom of the beaker, the mixer being set at a speed of 200 rounds per minute.
3. The specific compound is hydrotrope if the Octanoic Acid is completely solubilised, i.e. if the solution comprises only one phase, the phase being a liquid phase.

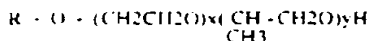
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It should be noted that in a preferred embodiment of the invention, the hydrotrope compound is a flowable material made of solid particles at operating conditions between 15 and 60° Celsius.

Hydrotrope compounds include the compounds listed thereafter:

A list of commercial hydrotropes could be found in McCutcheon's Emulsifiers and Detergents published by the McCutcheon division of Manufacturing Confectioners Company. Compounds of interest also include:

1. Nonionic hydrotrope with the following structure:

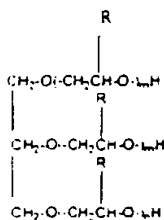


where R is a C2-C10 alkyl chain, x ranges from 1 to 15, y from 3 to 10

2. Anionic hydrotropes such as alkali metal aryl sulfonates. This includes alkali metal salts of benzoic acid, salicylic acid, benzenesulfonic acid and its many derivatives, naphthoic acid and various hydroaromatic acids. Examples of these are sodium, potassium and ammonium benzene sulfonate salts derived from toluene sulfonic acid, xylene sulfonic acid, cumene sulfonic acid, tetralin sulfonic acid, naphthalene sulfonic acid, methyl- naphthalene sulfonic acid, dimethyl naphthalene sulfonic acid, trimethyl naphthalene sulfonic acid=

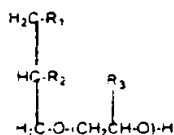
Other examples include salts of dialkyl benzene sulfonic acid such as salts of di-isopropyl benzene sulfonic acid, ethyl methyl benzene sulfonic acid, alkyl benzene sulfonic acid with an alkyl chain length with 3 to 10, (pref 4 to 9), linear or branched alkyl sulfonates with an alkyl chain with 1 to 18 carbons.

3. Solvent hydrotropes such as alkoxyated glycerines and alkoxyated glycerides, esters alkoxyated glycerines, alkoxyated fatty acids, esters of glycerin, polyglycerol esters. Preferred alkoxyated glycerines have the following structure



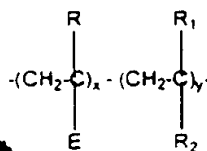
where l, m and n are each a number from 0 to about 20, with l+m+n = from about 2 to about 60, preferably from about 10 to about 45 and R represents H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>

Preferred alkoxyated glycerides have the following structure



where R<sub>1</sub> and R<sub>2</sub> are each C<sub>n</sub>COO or -(CH<sub>2</sub>CH(R<sub>3</sub>)-O)<sub>l</sub>-H where R<sub>3</sub> = H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> and l is a number from 1 to about 60, n is a number from about 6 to about 24.

4. Polymeric hydrotropes such as those described in EP636687:



where

E is a hydrophilic functional group.

R is H or a C1-C10 alkyl group or is a hydrophilic functional group.

R1 is H or a lower alkyl group or an aromatic group.

R2 is H or a cyclic alkyl or aromatic group.

The polymer typically has a molecular weight of between about 1000 and 1000000.

5 Hydrotrope of unusual structure such as 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (Diacid®)

Use of such compound in the invention would further increase the dissolution rate of the tablet, as a hydrotrope compound facilitates dissolution of surfactants, for example. Such a compound could be formed from a mixture or  
10 from a single compound

#### Tensile Strength

[0028] For the purpose of measuring tensile strength of a layer, the layer may be considered as a tablet itself

15 Depending on the composition of the starting material, and the shape of the tablets, the used compacting force may be adjusted to not affect the tensile strength, and the disintegration time in the washing machine. This process may be used to prepare homogenous or layered tablets of any size or shape. For a cylindrical tablet, the tensile strength corresponds to the diametral fracture stress (DFS) which is a way to express the strength of a tablet or layer, and is determined by the following equation:

$$\text{Tensile strength} = 2 F / \pi D t$$

25 Where F is the maximum force (Newton) to cause tensile failure (fracture) measured by a VK 200 tablet hardness tester supplied by Van Kell industries, Inc. D is the diameter of the tablet or layer, and t the thickness of the tablet or layer. For a non round tablet,  $\pi D$  may simply be replaced by the perimeter of the tablet.

(Method Pharmaceutical Dosage Forms: Tablets Volume 2 Page 213 to 217). A tablet having a diametral fracture stress of less than 20 kPa is considered to be fragile and is likely to result in some broken tablets being delivered to the consumer. A diametral fracture stress of at least 25 kPa is preferred.

30 This applies similarly to non cylindrical tablets, to define the tensile strength, whereby the cross section normal to the height of the tablet is non round, and whereby the force is applied along a direction perpendicular to the direction of the height of the tablet and normal to the side of the tablet, the side being perpendicular to the non round cross section

#### Tablet Dispensing

[0029] The rate of dispensing of a detergent tablet can be determined in the following way:

Two tablets, nominally 50 grams each, are weighed, and then placed in the dispenser of a Baucknecht® WA9850 washing machine. The water supply to the washing machine is set to a temperature of 20 °C and a hardness of 21 grains per gallon, the dispenser water inlet flow-rate being set to 8 l/min. The level of tablet residues left in the dispenser  
40 is checked by switching the washing on and the wash cycle set to wash program 4 (white/colors, short cycle). The dispensing percentage residue is determined as follows:

% dispensing = residue weight x 100 / original tablet weight

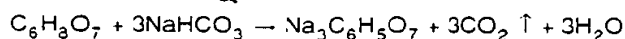
The level of residues is determined by repeating the procedure 10 times and an average residue level is calculated based on the ten individual measurements. In this stressed test a residue of 40 % of the starting tablet weight is  
45 considered to be acceptable. A residue of less than 30% is preferred, and less than 25% is more preferred

It should be noted that the measure of water hardness is given in the traditional "grain per gallon" unit, whereby 0.001 mole per litre = 7.0 grain per gallon, representing the concentration of  $\text{Ca}^{2+}$  ions in solution.

#### Effervescent

[0030] Detergent tablets may further comprise an effervescent.

Effervescency as defined herein means the evolution of bubbles of gas from a liquid, as the result of a chemical reaction between a soluble acid source and an alkali metal carbonate, to produce carbon dioxide gas, i.e.



Further examples of acid and carbonate sources and other effervescent systems may be found in: (Pharmaceutical



Dosage Forms Tablets Volume 1 Page 287 to 291)

An effervescent may be added to the tablet mix in addition to the detergent ingredients. The addition of this effervescent to the detergent tablet improves the disintegration time of the tablet. The amount will preferably be between 5 and 20% and most preferably between 10 and 20% by weight of the tablet. Preferably the effervescent should be added as an agglomerate of the different particles or as a compact, and not as separated particles.

Due to the gas created by the effervescency in the tablet, the tablet can have a higher D.F.S. and still have the same disintegration time as a tablet without effervescency. When the D.F.S. of the tablet with effervescency is kept the same as a tablet without, the disintegration of the tablet with effervescency will be faster.

Further dissolution aid could be provided by using compounds such as sodium acetate or urea. A list of suitable dissolution aid may also be found in Pharmaceutical Dosage Forms: Tablets, Volume 1, Second edition, Edited by H A Lieberman et al. ISBN 0-8247-8044-2.

#### Detergent surfactants

**[0031]** Surfactant are typically comprised in a detergent composition. The dissolution of surfactants is favoured by the addition of the highly soluble compound.

**[0032]** Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight include the conventional  $C_{11}$ - $C_{18}$  alkyl benzene sulfonates ("LAS") and primary, branched-chain and random  $C_{10}$ - $C_{20}$  alkyl sulfates ("AS"), the  $C_{10}$ - $C_{18}$  secondary (2,3) alkyl sulfates of the formula  $CH_3(CH_2)_x(CHOSO_3^-M^+)CH_3$  and  $CH_3(CH_2)_y(CHOSO_3^-M^+)CH_2CH_3$  where  $x$  and  $(y + 1)$  are integers of at least about 7, preferably at least about 9, and  $M$  is a water-solubilizing cation, especially sodium, unsaturated sulfates such as cleyl sulfate, the  $C_{10}$ - $C_{18}$  alkyl alkoxy sulfates ("AES"), especially EO 1-7 ethoxy sulfates,  $C_{10}$ - $C_{18}$  alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the  $C_{10}$ - $C_{18}$  glycerol ethers, the  $C_{10}$ - $C_{18}$  alkyl polyglycosides and their corresponding sulfated polyglycosides, and  $C_{12}$ - $C_{18}$  alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the  $C_{12}$ - $C_{18}$  alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and  $C_6$ - $C_{12}$  alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy),  $C_{12}$ - $C_{18}$  betaines and sulfobetaines ("sultaines"),  $C_{10}$ - $C_{18}$  amine oxides, and the like, can also be included in the overall compositions. The  $C_{10}$ - $C_{18}$  N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the  $C_{12}$ - $C_{18}$  N-methylglucamides. See WO 9 206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as  $C_{10}$ - $C_{18}$  N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl  $C_{12}$ - $C_{13}$  glucamides can be used for low sudsing.  $C_{10}$ - $C_{20}$  conventional soaps may also be used. If high sudsing is desired, the branched-chain  $C_{10}$ - $C_{16}$  soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts. In a preferred embodiment, the tablet comprises at least 5% per weight of surfactant, more preferably at least 15% per weight, even more preferably at least 25% per weight, and most preferably between 35% and 45% per weight of surfactant.

#### Non gelling binders

**[0033]** Non gelling binders can be integrated in detergent compositions to further facilitate dissolution.

If non gelling binders are used, suitable non-gelling binders include synthetic organic polymers such as polyethylene glycols, polyvinylpyrrolidones, polyacrylates and water-soluble acrylate copolymers. The handbook of Pharmaceutical Excipients second edition, has the following binders classification: Acacia, Alginic Acid, Carbomer, Carboxymethylcellulose sodium, Dextrin, Ethylcellulose, Gelatin, Guar gum, Hydrogenated vegetable oil type I, Hydroxyethyl cellulose, Hydroxypropyl methylcellulose, Liquid glucose, Magnesium aluminum silicate, Maltodextrin, Methylcellulose, polymethacrylates, povidone, sodium alginate, starch and zein. Most preferable binders also have an active cleaning function in the laundry wash such as cationic polymers, i.e. ethoxylated hexamethylene diamine quaternary compounds, bis-hexamethylene triamines, or others such as pentaamines, ethoxylated polyethylene amines, maleic acrylic polymers.

Non-gelling binder materials are preferably sprayed on and hence have an appropriate melting point temperature below 90°C, preferably below 70°C and even more preferably below 50°C so as not to damage or degrade the other active ingredients in the matrix. Most preferred are non-aqueous liquid binders (i.e. not in aqueous solution) which may be sprayed in molten form. However, they may also be solid binders incorporated into the matrix by dry addition but which have binding properties within the tablet.

Non-gelling binder materials are preferably used in an amount within the range from 0.1 to 15% of the composition, more preferably below 5% and especially if it is a non laundry active material below 2% by weight of the tablet.

It is preferred that gelling binders, such as nonionic surfactants are avoided in their liquid or molten form. Nonionic surfactants and other gelling binders are not excluded from the compositions, but it is preferred that they be processed into the detergent tablets as components of particulate materials and not as liquids.

## Builders

[0034] Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

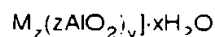
The level of builder can vary widely depending upon the end use of the composition.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the triphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. Examples of silicate builders are the alkali metal silicates, particularly those having a  $\text{SiO}_2\text{:Na}_2\text{O}$  ratio in the range 1.6 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839 issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- $\text{Na}_2\text{SiO}_5$  morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein but other such layered silicates, such as those having the general formula  $\text{NaMSi}_x\text{O}_{2x-1} \cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from 1 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include

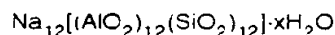
NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{SiO}_5$  (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669 Krummel, et al. issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ( $x = 0 - 10$ ) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

[0035] Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lambert et al. U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al. on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents

3,923,679; 3,835,163; 4,158,635; 4,120,374 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1,3,5-trihydroxy benzene-2,4,6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene-1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

[0036] Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 23, 1986. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include laurysuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions alone or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator. In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

#### Bleach

[0037] The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetrahydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al., filed June 3, 1985, European Patent Application 0,133,354, Banks et al., published February 20, 1985, and U.S. Patent 4,412,934, Chung et al., issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxydecanoic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers.

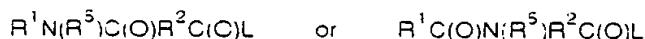
Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

[0038] Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators.

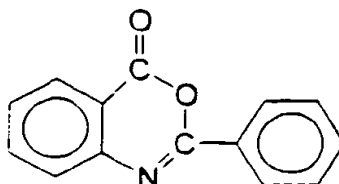
which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,554 issued April 10, 1990 to Mao et al. and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:

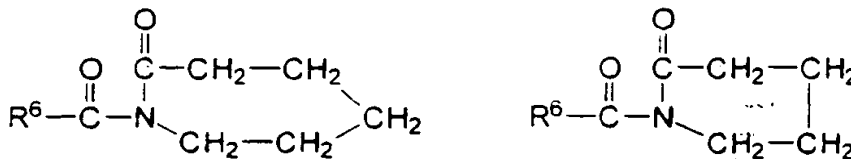


wherein  $R^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $R^2$  is an alkylene containing from 1 to about 6 carbon atoms,  $R^5$  is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate. Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723 issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein  $R^6$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonated zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2 and 544,490A1. Preferred examples of these catalysts include  $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(PF_6)_2$ ,  $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_2$ ,  $Mn^{IV}_4(u-O)_6(1,4,7\text{-tri-azacyclononane})_4(ClO_4)_4$ ,  $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(ClO_4)_3$ ,  $Mn^{IV}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})(OCH_3)_3(PF_6)$ , and mixtures thereof. Other metal-based bleach catalysts in-

clude those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,723,455; 5,234,944; 5,246,612; 5,256,779; 5,230,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

## Enzymes

**[0039]** Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

**[0040]** Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756 published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al. published January 9, 1985).

Amylases include, for example,  $\alpha$ -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al. issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2,075,028; GB-A-2,095,275 and DE-OS-2,247,832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487 laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WC 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al. issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985.

both Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,558, Horai et al. issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319 issued August 17, 1971 to Gedge et al. and European Patent Application Publication No. 0 199 405, Application No. 86200526.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

[0041] Other components which are commonly used in detergent compositions and which may be incorporated into detergent tablets include chelating agents, soil release agents, soil antiredeposition agents, dispersing agents, suds suppressors, fabric softeners, dye transfer inhibition agents and perfumes.

[0042] The compounds disclosed above for a product are advantageously packed in a packaging system. A packaging system may be formed from a sheet of flexible material. Materials suitable for use as a flexible sheet include mono-layer, co-extruded or laminated films. Such films may comprise various components, such as poly-ethylene, poly-propylene, poly-styrene, poly-ethylene-terephthalate. Preferably, the packaging system is composed of a poly-ethylene and bi-oriented-polypropylene co-extruded film with an MVTR of less than 5 g/day/m<sup>2</sup>. The MVTR of the packaging system is preferably of less than 10 g/day/m<sup>2</sup>, more preferably of less than 5 g/day/m<sup>2</sup>. The film (2) may have various thicknesses. The thickness should typically be between 10 and 150 µm, preferably between 15 and 120 µm, more preferably between 20 and 100 µm, even more preferably between 25 and 80 µm and most preferably between 30 and 40 µm.

A packaging material preferably comprises a barrier layer typically found with packaging materials having a low oxygen transmission rate, typically of less than 300 cm<sup>3</sup>/m<sup>2</sup>/day, preferably of less than 150 cm<sup>3</sup>/m<sup>2</sup>/day, more preferably of less than 100 cm<sup>3</sup>/m<sup>2</sup>/day, even more preferably of less than 50 cm<sup>3</sup>/m<sup>2</sup>/day and most preferably of less than 10 cm<sup>3</sup>/m<sup>2</sup>/day. Typical materials having such barrier properties include bi-oriented polypropylene, polyethylene terephthalate, Nylon, poly(ethylene vinyl alcohol) or laminated materials comprising one of these, as well as SiO<sub>x</sub> (Silicon oxides), or metallic foils such as aluminium foils for example. Such packaging material may have a beneficial influence on the stability of the product during storage for example. Among the packing method used are typically the wrapping methods disclosed in WO92/20593, including flow wrapping or over wrapping. When using such processes, a longitudinal seal is provided which may be a fin seal or an overlapping seal, after which a first end of the packaging system is closed with a first end seal, followed by closure of the second end with a second end seal.

The packaging system may comprise re-closing means as described in WO92/20593. In particular, using a twist, a cold seal or an adhesive is particularly suited. Indeed, a band of cold seal or a band of adhesive may be applied to the surface of the packaging system at a position adjacent to the second end of the packaging system, so that this band may provide both the initial seal and re-closure of the packaging system. In such a case the adhesive or cold seal band may correspond to a region having a cohesive surface, i.e. a surface which will adhere only to another cohesive surface. Such re-closing means may also comprise spacers which will prevent unwanted adhesion. Such spacers are described in WO 95/13225, published on the 18<sup>th</sup> of May 1995.

There may also be a plurality of spacers and a plurality of strips of adhesive material. The main requirement is that the communication between the exterior and the interior of the package should be minimal, even after first opening of the packaging system. A cold seal may be used, and in particular a grid of cold seal, whereby the cold seal is adapted so as to facilitate opening of the packaging system.

## EXAMPLES

### Example 1

#### [0043]

i) A detergent base powder of composition A was prepared as follows: all the particulate material of base composition were mixed together in a mixing drum or spray drum to form a homogenous particulate mixture, apart from the binder spray-on system, the fluorescer or brightener, and the photobleach Zinc Phthalocyanine sulphonate. The particulate mixture was thereafter divided in two equal parts, one part for making a white layer, another part for making a green layer. The white layer material is obtained by spraying the brightener or fluorescer together with half of the binder. The green layer material is obtained by spraying the photobleach Zinc Phthalocyanine sulphonate together with the rest of the binder. The layer were then processed independently in a Loedige KM 600®.

ii) Using a Bonals® rotary press both matrices were filled in two independent force feeding flasks. Both layers are compressed together in the precompression and compression stations to form a dual layer tablet.

iii) In this particular example, the tablets have a square cross section of 45 mm side, a height of 24 mm and a weight of 45 gr. The height of the green bottom layer corresponded to 50% of the total height of the tablet. The

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tensile strength of the uncoated tablets was 13 kpa.

iv) The tablet was thereafter coated with 2.5 g of coating formed from 90% by weight of acrylic acid and 10% by weight of Nymcel-ZSB16™ by Metsa Serla

	Composition A
	(%)
Anionic agglomerates 1	9.1
Anionic agglomerates 2	22.5
Nonionic agglomerates	9.1
Cationic agglomerates	4.6
Layered silicate	9.7
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	7.67
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.6
Soil Release Polymer	0.3
Fluorescer	0.2
Zinc Phthalocyanine sulphonate	0.03
Soap powder	1.2
Suds suppressor	2.8
Citric acid	5.5
Protease	1
Lipase	0.35
Cellulase	0.2
Amylase	1.1
Binder spray-on system	4.75
Perfume spray-on	0.5

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate

Nonionic agglomerate comprise 26% nonionic surfactant, 6% Lutensil K-HD 96, 40% Sodium acetate anhydrous, 20% carbonate and 8% zeolite.

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

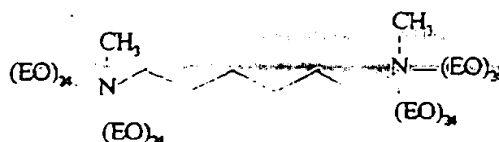
Layered silicate comprises of 95% SKS 6 and 5% silicate

Bleach activator agglomerates comprise of 31% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning), 59% of zeolite and 29.5% of water.

Binder spray-on system comprises 16% by weight of polymer of the following kind:



68 % by weight of PEG4000 and 16% by weight of DIBS (Sodium di isoalkylbenzene sulphonate or Sodium toluene sulphonate).

[0044] An other example of a composition which may have been used is as follows:

	Composition B
	(%)
Anionic agglomerates 1	9.1
Anionic agglomerates 2	22.5
Nonionic agglomerates	9.1
Cationic agglomerates	4.6
Layered silicate	9.7
Sodium percarbonate	12.2
Bleach activator agglomerates	6.1
Sodium carbonate	7.67
EDDS/Sulphate particle	0.5
Tetrasodium salt of Hydroxyethane Diphosphonic acid	0.6
Soil Release Polymer	0.3
Fluorescer	0.2
Zinc Phthalocyanine sulphonate	0.03
Soap powder	1.2
Suds suppressor	2.8
Citric acid	5.5
Protease	1
Lipase	0.35
Cellulase	0.2
Amylase	1.1
Binder spray-on system	4.75
Perfume spray-on	0.5

Anionic agglomerates 1 comprise of 40% anionic surfactant, 27% zeolite and 33% carbonate

Anionic agglomerates 2 comprise of 40% anionic surfactant, 28% zeolite and 32% carbonate

Nonionic agglomerate comprise 26% nonionic surfactant, 6% Lutensit K-HD 96, 40% Sodium acetate anhydrous, 20% carbonate and 8% zeolite.

Cationic agglomerates comprise of 20% cationic surfactant, 56% zeolite and 24% sulphate

Layered silicate comprises of 95% SKS 6 and 5% silicate

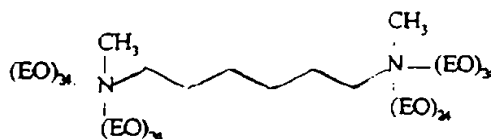
Bleach activator agglomerates comprise of 31% TAED, 17% acrylic/maleic copolymer (acid form) and 2% water.

Ethylene diamine N,N-disuccinic acid sodium salt/Sulphate particle comprise of 58% of Ethylene diamine N,N-disuccinic acid sodium salt, 23% of sulphate and 19% water.

Suds suppressor comprises of 11.5% silicone oil (ex Dow Corning), 59% of zeolite and 29.5% of water.



Binder spray-on system comprises 16% by weight of polymer of the following kind.



68 % by weight of: PEG4000 and 16% by weight of: DIBS (Sodium di isoalkylbenzene sulphonate or Sodium toluene sulphonate)

#### Example 2

##### [0045]

- i) A detergent base powder of composition A was prepared as follows: all the particulate material of base composition were mixed together in a mixing drum or spray drum to form a homogenous particulate mixture, apart from the binder spray-on system, the fluorescer or brightener, and the photobleach Zinc Phthalocyanine sulphonate. The particulate mixture was thereafter divided in two equal parts, one part for making a white layer, another part for making a green layer. The white layer material is obtained by spraying the brightener or fluorescer together with half of the binder. The green layer material is obtained by spraying the photobleach Zinc Phthalocyanine sulphonate together with the rest of the binder. The layer were then processed independently in a Loedige-KM 600®.
- ii) Using a Bonals® rotary press both matrices were filled in two independent force feeding flasks. Both layers are compressed together in the precompression and compression stations to form a dual layer tablet.
- iii) In this particular example, the tablets have a square cross section of 45 mm side, a height of 24 mm and a weight of 45 gr. The height of the green bottom layer corresponded to 50% of the total height of the tablet. The tensile strength of the uncoated tablets was 13 kpa.
- iv) The tablet was thereafter coated with 2.5 g of coating formed from 90% by weight of adipic acid and 10% by weight of Bentonite clay from CSM.

#### Example 3

##### [0046]

- i) A detergent base powder of composition A was prepared as follows: all the particulate material of base composition was mixed together in a mixing drum or spray drum to form a homogenous particulate mixture. The binder system was then sprayed on. The powder were then processed in a Loedige KM 600®.
- ii) Using a Instron® Laboratory bench press, detergent powder was filled in the die. The powder had been compressed with a force so that the tensile strength of the tablet was 10kpa.
- iii) In this particular example, the tablets have a diameter of 54 mm side, a height of 24 mm and a weight of 45 gr.
- iv) The tablet was thereafter coated with 2.5 g of coating formed from 90% by weight of Adipic acid and 10% by weight of bentonite clay from CSM.

#### Example 4

##### [0047]

- i) A detergent base powder of composition A was prepared as follows: all the particulate material of base composition were mixed together in a mixing drum or spray drum to form a homogenous particulate mixture. The binder system was then sprayed on. The powder were then processed in a Loedige KM 600®.
- ii) Using a Instron® Laboratory bench press, detergent powder was filled in the die. The powder had been compressed with a force so that the tensile strength of the tablet was 10kpa.
- iii) In this particular example, the tablets have a diameter of 54 mm side, a height of 24 mm and a weight of 45 gr.

The tablet was thereafter coated with 2.5 g of coating formed from 85% by weight of Adipic acid, 10% by weight of bentonite clay from and 1% of Coasol™

## Example 5

[0048]

- i) A detergent base powder of composition A was prepared as follows: all the particulate material of base composition were mixed together in a mixing drum or spray drum to form a homogenous particulate mixture. The binder system was then sprayed on. The powder was then processed in a Loedige KM 600®.
- ii) Using a Instron® Laboratory bench press, detergent powder was filled in the die. The powder had been compressed with a force so that the tensile strength of the tablet was 10kpa.
- iii) In this particular example the tablets have a diameter of 54 mm side, a height of 24 mm and a weight of 45 gr

The tablet was thereafter coated with 2.5 g of coating formed from 37% by weight of Adipic acid, 10% by weight of bentonite clay from and 1% of Coasol™ and 2 % of Soika-Floc™ 1016.

## Results

[0049] It was observed that:

[0050] For about 500 tablets made for each of examples 1 and 2, when a coated tablet is fully immersed in 1 litre of city water at 20°C, the coating disintegrates in about 25 seconds for example 1, and in about 3 seconds for example 2

[0051] Furthermore, by comparing 10 tablets made according to example 3, 4 and 5, it was observed the following coating splitting occurrence:

	Example 3	Example 4	Example 5
Splitting occurrence (Tablets of 10kpa when non-coated)	100%	20%	0%

## Claims

1. A coated detergent tablet, the coating comprising an acid having a melting temperature of at least 145°C, whereby the coating further comprises a clay.
2. A coated detergent tablet according to claim 1, whereby the coating comprises a component which is liquid at 25°C.
3. A tablet according to claim 2 wherein the coating further comprises a crystallised structure.
4. A tablet according to claim 3 wherein the material forming the crystallised structure is a dicarboxylic acid.
5. A tablet according to any of claims 1 or 4 wherein the coating consists essentially of adipic acid.
6. A tablet according to claim 1, whereby the coating further comprises reinforcing fibres.
7. A tablet according to claim 1, whereby the clay is in particles having a size below 75µm diameter.
8. A process for making a tablet according to any of the above claims comprising the steps of
  - (a) forming a core by compressing a particulate material, the particulate material comprising surfactant and detergent builder;
  - (b) applying a coating material to the core, the coating material being in the form of a melt;
  - (c) allowing the molten coating material to solidify;
 characterised in that the coating comprising an acid having a melting temperature of at least 145°C, whereby the coating further comprises a clay.
9. A process for making a tablet according to any of claims 1 to 7 comprising the steps of:
  - (a) forming a core by compressing a particulate material, the particulate material comprising surfactant and detergent builder;

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- (b) applying a coating material to the core, the coating material being dissolved in a solvent or water
- (c) allowing the solvent or water to evaporate.

characterised in that the coating comprising an acid having a melting temperature of at least 145°C, whereby the coating further comprises a clay.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 37 0017

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D.X	EP 0 846 756 A (PROCTER & GAMBLE) 10 June 1998	1-5.3.9	C11D17/00
A	* claims 1.2.5-7; examples * * page 3, line 44 - page 4, line 21 *	6.7	C11D3/12 C11D3/20
D.X	EP 0 846 755 A (PROCTER & GAMBLE) 10 June 1998	1-5.3.9	
A	* claims; examples * * page 3, line 51 - page 4, line 27 *	6.7	
D.X	EP 0 846 754 A (PROCTER & GAMBLE) 10 June 1998	1-5.3.9	
A	* page 3, line 42 - page 4, line 11 * * claims; examples *	6.7	
D.A	EP 0 716 144 A (UNILEVER PLC. ) 12 June 1996	1.9	
A	* claims; examples * EP 0 875 558 A (ECOLAB INC. ) 4 November 1998	1.6.7.9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	* column 2, line 38 - column 3, line 5 * * column 3, line 25 - column 6, line 17 *		C11D
The present search report has been drawn up for all claims			

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 June 1999	Serbetsoglou, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X particularly relevant taken alone Y particularly relevant in combination with another document of the same category A technical background C non-written disclosure P intermediate document</p> <p>E theory or principle underlying the invention F earlier patent document, but published on or after its filing date D document cited in the application I document cited for other reasons G member of the same patent family corresponding document</p>		

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 99 37 0017

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on the European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-06-1999

Patent document cited in search report		Publication date	Patent family members	Publication date
EP 0846756	A	10-06-1998	AU 5443698 A	29-06-1998
			WO 9824873 A	11-06-1998
EP 0846755	A	10-06-1998	AU 5443898 A	29-06-1998
			WO 9824875 A	11-06-1998
EP 0846754	A	10-06-1998	AU 7625098 A	29-06-1998
			WO 9824874 A	11-06-1998
EP 0716144	A	12-06-1996	NONE	
EP 0673558	A	04-11-1998	CA 2236014 A	30-10-1998

For more details about this annex see Official Journal of the European Patent Office, No. 12/82

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